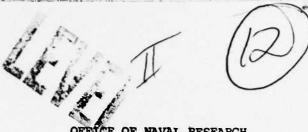OFFICE OF NAVAL RESEARCH

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Classical Stochastic Model of Laser-Stimulated
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Laser Excitation via Multiphonon Couplings

by

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20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

The dynamical behavior of laser-stimulated surface processes (LSSP) is studied by the generalized Langevin equation via the memory effects of the damping kernel, the dephasing kernel and mode-mode interactions. The temperature-dependent averaged energy absorption rate (which characterizes the line shape) is calculated by solving the Laplace-Fourier transform of the velocity correlation function. The features of the response function and its overall line broadening are discussed in terms of Markovian processes. The nature of LSSP and laser-selective effects are discussed in

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Classical Stochastic Model of Laser-Stimulated
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Laser Excitation via Multiphonon Couplings[*]

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The dynamical behavior of laser-stimulated surface processes (LSSP) is studied by the generalized Langevin equation via the memory effects of the damping kernel, the dephasing kernel and mode-mode interactions. The temperature-dependent averaged energy absorption rate (which characterizes the line shape) is calculated by solving the Laplace-Fourier transform of the velocity correlation function. The features of the response function and its overall line broadening are discussed in terms of Markovian processes. The nature of LSSP and laser-selective effects are discussed in terms of the multiphonon coupling strength and the related "internal resonant" condition. It is shown that laser-selective bond breaking is possible for a slow intramolecular vibrational relaxation rate which is governed by a high-order multiphonon process or a far off "internal resonance."

I. Introduction

Two general problems in laser-stimulated surface processes (LSSP) are: (i) the dynamical behavior of the excited adspecies/ surface system and (ii) the selective and nonselective nature of LSSP.[1-6] The latter problem was recently studied by a quantum model where the energy populations of a multilevel system were numerically analyzed for different sets of the pumping rate, the relaxation rate and the damping factor.[5,6] The energy absorption profiles were also studied by the classical Langevin theory, where the many-body effects of the bath modes are effectively replaced by the bath-induced damping factor and frequency shift in the Wigner-Weisskopf-type approximation.[7] In the present paper, we shall further study these two major problems of LSSP via the generalized Langevin equation (GLE) and the multiphonon coupling strength with the related "internal resonant" condition.[8,9]

The relaxation dynamics of LSSP described by GLE with memory effects is presented in Section II, and the temperature-dependent averaged energy absorption rate for the model systems of (i) a single active mode and (ii) two coupled active modes is calculated in Section III. In Section IV, we analyze the nature of laser-selective effects via multiphonon processes and derive (by a classical model) the required condition for a rapid intramolecular relaxation. The averaged energy absorption rate of a system with many active modes is derived (by a quantum model) in the Appendix.

II. Generalized Langevin Equation and Relaxation Dynamics

We consider a heterogeneous model system consisting of species (atoms or molecules) chemisorbed on a solid surface and subject to low-power infrared laser radiation. The Lagrangian of the system may be written as

$$\mathcal{L}(Q_1, Q_2, \cdots Q_N) = \frac{1}{2} \sum_{i=1} m_i (\dot{Q}_i^2 - \Omega_i^2 Q_i^2) + \sum_i f_i(t) Q_i - V_{anh}(Q_1, Q_2, \cdots Q_N) . \quad (1)$$

where Q_i ($i = 1, 2, \cdots, N$) are the normal coordinates of the system (with normal mode frequencies Ω_i). $f_i(t)$ is the transformed generalized force given by

$$f_i(t) = q_i E_i \cos(\omega t) , \quad (2)$$

where E_i is the effective electric field of the laser radiation acting on the i-th normal mode (with classical charge q_i). $V_{anh}(Q_1, Q_2, \cdots, Q_N)$ is the anharmonic mode-mode coupling potential given by[7]

$$V_{anh} = \sum_{ij} \lambda_{ij} Q_i Q_j + \sum_{ijk} \lambda_{ijk}^{(2)} Q_i Q_j Q_k + \sum_p \sum_{ij} \lambda_{ij}^{(p)} Q_i Q_j^p + \cdots , \quad (3)$$

where λ_{ij} and $\lambda_{ij}^{(p)}$ are the coupling constants characterizing the single-phonon and multiphonon processes, respectively. The equations of motion,

$$\frac{d}{dt} \left(\frac{\partial \mathcal{L}}{\partial \dot{Q}_i} \right) - \frac{\partial \mathcal{L}}{\partial Q_i} = 0, \quad i = 1, 2, \cdots, N , \quad (4)$$

are a set of coupled nonlinear equations. As pointed out in a previous paper,[7] the numerical solution of the above equations involves long computation times due to the high frequency of the laser field ($\omega \sim 10^{14}$ sec^{-1}), where the time scale of the energy absorption profiles is much longer than the oscillation cycle of the field for the low-power excitation processes. A new set of transformed equations in the rotating frame was developed to over-

come such numerical difficulty.[7] However, for a three-dimensional solid system, the low-frequency bulk-phonon modes are condensed and give us essentially an infinite number of normal modes, where any numerical method will be unfavorable.

For tractable results, we shall model the system in the frequency domain as follows: one (or more than one) of the vibrational modes of the total system, which strongly interacts with the laser field, may be singled out as the pumped active (A) mode, and the remaining modes are divided into two subsystems: the surface-phonon (B) modes (with high frequencies) and the bulk-phonon (C) modes (with condensed low frequencies). The condensed C modes are considered to provide a heat bath for the (A + B) modes. By employing the Wigner-Weisskopf-type approximation, the many-body effects of the condensed C modes may be replaced by introducing a damping factor and a frequency-shift in the A and B modes. Instead of the coupled Equations (4), we thus may describe laser-stimulated surface processes by the generalized Langevin equation (GLE) as follows:[10]

$$
f_j(t) + f_j^R(t) = m_j \ddot{Q}_j(t) + m_j \int_0^t \beta_j(t-t') \dot{Q}_j(t') \, dt' + m_j \bar{\Omega}_j^2 \int_0^t M_j(t-t') \dot{Q}_j(t') \, dt'
$$
$$
- \sum_{i \neq j} \int_0^t N_{ij}(t-t') \dot{Q}_i(t') \, dt' . \tag{5}
$$

Q_j is the j-th normal coordinate of the (A + B) subsystem; $\beta_j(h)$ and $M_j(t)$ are the damping kernel and the dephasing kernel, respectively, describing the interaction dynamics among the (A + B) modes and the bath (C) modes; $N_{ij}(t)$ is the interaction function between the i-th and j-th modes; $f_j(t)$ and $f_j^R(t)$ are the driving force of the laser field and the bath-induced random force acting on the j-th mode, respectively; and $\bar{\Omega}_j$ is the effective frequency of the j-th mode related to the fundamental frequency (Ω_j) of isolated (A + B) sub-

system, the anharmonicity (K_j^*) and the bath-induced frequency shift ($\delta\omega_j$) by

$$\bar{\Omega}_j = \Omega_j - K_j^* A_j^2 - \delta\omega_j \quad , \tag{6}$$

where A_j is the steady-state amplitude of the j-th mode and is proportional to the applied laser field intensity.[4,11]

The above GLE with memory effects enables us to study the dynamics of LSSP via the T_1 energy relaxation [governed by the damping kernel $\beta_j(t)$] and the anharmonic mode-mode interaction function $N_{ij}(t)$. We note that the damping kernel characterizes the dynamics of the energy relaxation of the excited mode and the energy feedback from the bath modes, while the dephasing kernel characterizes the bath-induced dephasing of the excited mode in which the energy population does not change. The major mechanisms which cause the T_1 and T_2 relaxations are: (i) vibration-induced lattice-site transitions of the adspecies; (ii) anharmonic mode-mode coupling of the (A + B) subsystem and its coupling with the bath modes; (iii) the interspecies indirect interactions(via surface-phonon modes); (iv) the fluctuation of the effective dipole of the active mode; and (v) the amplitude and direction fluctuation of the effective electric field acting on the normal coordinate of the system caused by the electron charge transfer and the libration of the adspecies. [For a more detailed discussion on the overall line broadening, see Ref. 3.]

III. Temperature-Dependent Energy Absorption Rate

Here we apply the GLE described in the previous section to the calculation of the energy absorption rate of the system. Two model systems are considered: (1) there is only one active mode in

the (A + B) subsystem which coupled to the bath modes, and (2) there are two coupled active modes in the (A + B) subsystems and both are coupled to the bath modes.

By linear response theory and time-dependent perturbation theory, we may express the temperature-dependent averaged energy absorption rate of the system (via the active dipoles) as follows (see the Appendix for the derivation):

$$\overline{\left\langle \frac{d\mathcal{E}}{dt} \right\rangle} = \left(\frac{1 - e^{-\beta \hbar \omega}}{2 \hbar \omega} \right) \sum_{i,j} \left(q_i q_j E_i E_j \right) \left(R_e \ F_{ij}[\omega] \right) , \qquad (7)$$

where $F_{ij}[\omega]$ is the Laplace-Fourier transform of the velocity correlation function defined by

$$F_{ij}[\omega] \equiv \int_0^\infty e^{-i\omega t} F_{ij}(t) \, dt \quad , \qquad (8.2)$$

$$F_{ij}(t) = \left\langle \dot{Q}_i(t) \dot{Q}_j(0) \right\rangle \quad . \qquad (8.1)$$

Thus, we see that for a system with more than one active mode, the total absorption line shape is a linear combination of the individual line shapes ($F_{ii}[\omega]$) plus the interference term ($F_{ij}[\omega]$, $i \neq j$), characterized by the Laplace-Fourier transforms of the velocity correlation functions $F_{ij}(t)$ which will be computed from the GLE [Eq.(5)].

A. Single Active Mode System

The GLE [Eq.(5)] in this single active mode case reduces to

$$m \ddot{Q}(t) + m \int_0^t \beta(t-t') \dot{Q}(t') dt' + m \bar{\Omega}^2 \int_0^t M(t-t') \dot{Q}(t') dt' = f(t) + f^R(t) , \quad (9)$$

and the averaged energy absorption rate [Eq.(7)] is simply

$$\overline{\left\langle \frac{d\mathcal{E}}{dt} \right\rangle} = \frac{(qE)^2}{2\hbar\omega} \left(1 - e^{-\beta\hbar\omega} \right) \left(R_e \ F[\omega] \right) . \qquad (10)$$

We now solve the velocity autocorrelation function $F(t) \equiv \langle \dot{Q}(t)\dot{Q}(0) \rangle$

which is governed by the GLE in the absence of the laser field. By multiplying both sides of Eq.(9) by $\dot{Q}(0)$ and performing the ensemble average over the initial conditions, we obtain

$$\dot{F}(t) + \int_0^t \beta(t-t') F(t') dt' + \int_0^t M(t-t') F(t') dt' = 0. \qquad (11)$$

Here we have made use of the fluctuation-dissipation theorem [12] and assumed a white-noise process:

$$F(0) = kT_0/m, \quad \langle \dot{Q}(0) f^R(t) \rangle = 0. \qquad (12)$$

By taking the Laplace-Fourier transform of Eq.(12), we find

$$F[\omega] = \frac{kT_0}{m} \left[\frac{1}{i\omega + \beta[\omega] + \tilde{\Omega}^2 M[\omega]} \right], \qquad (13)$$

where $\beta[\omega]$ and $M[\omega]$ are the Laplace-Fourier transforms of the damping kernel $\beta(t)$ and the dephasing kernel $M(t)$, respectively. In obtaining Eq.(13), we have used the equilibrium average, $F(0) \equiv \langle \dot{Q}(0) \dot{Q}(0) \rangle = kT_0/m$, and the convolution theorem for the Laplace-Fourier transform.

For given forms of the memory functions $\beta(t)$ and $M(t)$, we shall be able to find the related Laplace-Fourier transform and in turn compute the averaged energy absorption rate by the real part of $F[\omega]$. We note that in using the convolution theorem, we require the memory functions $\beta(t)$ and $M(t)$ and the velocity auto-correlation function $F(t)$ to be well behaved, i.e., $\beta(t)$, $M(t)$, $F(t) \to 0$, as $t \to \infty$. The damping kernel which governs the T_1 energy relaxation and affects the energy population of the active mode is chosen in the form[13]

$$\beta(t) = \beta_0 e^{-(1/2)\Gamma t} \left[\cos(\omega_1 t) + \tfrac{1}{2}\Gamma \omega_1^{-1} \sin(\omega_1 t) \right], \qquad (14)$$

where β_0 is the initial damping kernel with the decay constant Γ

and the oscillation frequency $\omega_1 = [\bar{\Omega}^2 - (\Gamma/2)^2]^{1/2}$. Thus damping kernel satisfies the equation

$$\ddot{\beta}(t) + \Gamma\dot{\beta}(t) + \bar{\Omega}^2\beta(t) = 0 \tag{15}$$

for the underdamping case (i.e., $\Gamma < 2\bar{\Omega}$) with the boundary conditions $\beta(0) = \beta_0$ and $\dot{\beta}(0) = 0$.

We note that this oscillating-type damping kernel contains the memory effects of the T_1 energy relaxation processes, where the excitation and relaxation processes of the active mode are accompanied by the energy feedback of the bath modes. Such memory effects may be significantly important when the bath modes are only slightly excited at the initial stage of the multiphonon relaxation process where the correlation time of the bath modes is comparable to the radiative rate.[14] When the bath modes are highly "heated" due to the rapid energy randomization among these modes where the correlation time is much faster than all the other time scales of the processes, the damping kernel $\beta(t)$ loses all memory effects and the T_1 energy relaxation processes are irreversible. This is the case of Markovian processes, whereby the damping kernel [Eq.(14)] reduces to a Dirac delta function

$$\beta(t) = \gamma_1 \delta(t) , \tag{16.a}$$

$$\gamma_1 = \lim_{\substack{\beta_0 \to \infty \\ \Gamma \to \infty}} (\beta_0/\Gamma) , \tag{16.b}$$

where γ_1 is a constant damping factor which may be related to the microscopic multiphonon coupling strength and the Boson occupation number of the bath modes [see Eq.(34)].

The T_2 dephasing kernel $M(t)$ which destroys the coherent

nature of the excitation (i.e., the stochastic modulation of the
fluctuating frequency of the active mode), but does not change
the energy population, is chosen in an exponential form[8,15]

$$M(t) = exp(-\gamma_2 t) \tag{17}$$

where γ_2 is the dephasing-induced line broadening related to the
phase coherent time, τ_c, by $\gamma_2 = \tau_c^{-1}$. Working out the Laplace-
Fourier transforms of the memory functions, $\Lambda[\omega]$ and $M[\omega]$, and
substituting the results into Eq.(13), we obtain, from the real
part of $F[\omega]$, the temperature-dependent averaged energy absorption
rate [Eq.(10)].

$$\overline{\langle \frac{d\varepsilon}{dt} \rangle} = (\mu E)^2 P(T_0) \left[\frac{(\gamma_2 D' - \omega^2)R + \omega(D' + \gamma_2\Gamma)S}{R^2 + S^2} \right] . \tag{18}$$

where

$$P(T_0) = \frac{1}{2\hbar\omega}(1 - e^{-\hbar\omega/kT_0}), \tag{19}$$

$$R = D'(D + \gamma_2\omega) + \beta_0(\gamma_2\Gamma - \omega^2), \tag{20a}$$

$$S = \Gamma\omega(D + \gamma_2\omega) + \beta_0\omega(\gamma_2 + \Gamma), \tag{20b}$$

$$D' = D^2 + (\Gamma/2)^2, \tag{20c}$$

$$D = \bar{\Omega}^2 - \omega^2. \tag{20d}$$

This reflects a rather general line shape of the system, where
memory effects of the energy relaxation and the partially coherent
nature of the excitation processes are characterized by the damping
kernel parameters β_0 and Γ and the dephasing rate γ_2.

For tractable results of the overall line broadening, let
us consider the Markovian limiting case, i.e., $\beta(t) = \beta_0\delta(t)$. The
averaged energy absorption rate Eq.(18) reduces to the simple form

$$\overline{\left\langle \frac{d\varepsilon}{dt} \right\rangle} = (q_0^s E)^2 P(T_0) \left[\frac{\gamma_2 A + \omega B}{A^2 + B^2} \right] , \qquad (21)$$

$$A = \bar{\Omega}^2 - \omega^2 + \gamma_1 \gamma_2 , \qquad (22.A)$$

$$B = \omega (\gamma_1 + \gamma_2) . \qquad (22.b)$$

The important features of the above temperature-dependent line shape are: (1) for low temperature ($kT_0 \ll \hbar\omega$), $P(T_0)$ is independent to T_0 when the overall broadening ($\gamma_1 + \gamma_2$) is weakly temperature-dependent [in general, γ_1 is temperature-dependent - see Eq.(34)]; (2) the asymmetric line shape is due to the dephasing term γA which is antisymmetric with respect to $\bar{\omega} = \bar{\Omega} + (\gamma_1\gamma_2)/(2\bar{\Omega})$, i.e., $A > 0$ when $\omega < \bar{\omega}$, and $A < 0$ when $\omega > \bar{\omega}$; and (3) for $\gamma_1\gamma_2 \ll \omega$, Eq.(21) reduces to essentially a Lorentzian with the FWHM = $\gamma_1 + \gamma_2$, where for low excitations (coherent processes), the overall line broadening is dominant by γ_1, while for high excitations (incoherent processes) the strong interactions between the active mode and the dense bath modes destroy the coherent nature of the excitations, and the T_2 dephasing broadening (γ_2) is dominant. We note that the simple additive nature of the overall broadening [the ($\gamma_1 + \gamma_2$) term in Eq.(21)] is available only for the Markovian processes, where the correlation time of the bath modes is much faster than the T_1 and T_2 relaxation rates and the memory effects of the damping kernel are not significant. We believe that the dynamical transition of the nature of LSSP (from a coherent to an incoherent excitation) may be described by the relative magnitudes of the relaxation parameters β_0, Γ and γ_2 contained in the line shape [Eqs.(18) and (21)], which reflects

not only the internal level structure of the active mode (which is characterized by the conformation of the adspecies and the heterogeneity of adsorbent) but also the dynamical behavior of the excited adspecies, e.g., vibration-induced surface migration, surface recombination and the rate processes.[3]

B. <u>Two-Coupled Active Modes</u>

For the situation that there are two active modes with frequencies close together (within the detuning range of the field), then both modes will strongly interact with the field. While acting with each other (via linear coupling), these two modes both are coupled to the bath modes (via multiphonon processes), and the energy deposited in the active modes will gradually relax to the bath modes. At steady-state, the energy stored in the active modes remains unchanged and the averaged energy absorption rate of the system must equal the energy dissipative rate of the active modes. We may express this steady-state averaged power absorption classically by[16]

$$\overline{\langle \frac{d\mathcal{E}}{dt} \rangle} = \overline{\sum_{i=1,2} f_i(t) \dot{Q}_i(t)} = \overline{P}_1 + \overline{P}_2 + \overline{P}_{12} , \qquad (23)$$

where $f_i(t)$ is the generalized force for the normal coordinate Q_i governed by the usual Langevin equation (without including the memory effects); $\overline{p}_1$ and $\overline{p}_2$ are the averaged power absorption for the uncoupled active modes and $\overline{p}_{12}$ is the interference term due to their couplings.

For a quantum system with memory effects, instead of Eq.(23), the (time and ensemble) averaged power absorption is given by [from Eq.(7)]

$$\overline{\langle \frac{d\mathcal{E}}{dt} \rangle} = \overline{\langle \dot{P}_{11} \rangle} + \overline{\langle \dot{P}_{22} \rangle} + \overline{\langle \dot{P}_{12} \rangle} + \overline{\langle \dot{P}_{21} \rangle} , \tag{24}$$

$$\overline{\langle \dot{P}_{ij} \rangle} = P(T_0) \left(q_i q_j E_i E_j \right) \left(Re\, F_{ij}[\omega] \right) , \tag{25}$$

which is similar to that of the classical expression, except that
here we take the ensemble average $\langle \cdots \rangle$ over the quantum states,
and the instantaneous velocity $\dot{Q}(t)$ is replaced by its correlation
function $F_{ij}(t) \equiv \langle \dot{Q}_i(t)\dot{Q}_i(0) \rangle$ due to the memory kernels.

To obtain the above quantity, we first consider the GLE
[Eq.(5)] for the case of two coupled active modes:

$$\ddot{Q}_1(t) + \int_0^t \beta_1(t-t')\dot{Q}_1(t')dt' + \bar{\Omega}_1^2 \int_0^t M_1(t-t')\dot{Q}_1(t)dt' - \frac{1}{m_1}\int_0^t N_{12}(t-t')\dot{Q}_2(t')dt' = \left[f_1(t) + f_1^R(t) \right]/m_1 , \tag{26}$$

$$\ddot{Q}_2(t) + \int_0^t \beta_2(t-t')\dot{Q}_2(t')dt' + \bar{\Omega}_2^2 \int_0^t M_2(t-t')\dot{Q}_2(t')dt' - \frac{1}{m_2}\int_0^t N_{12}(t-t')\dot{Q}_1(t')dt' = \left[f_2(t) + f_2^R(t) \right]/m_2 . \tag{27}$$

By multiplying both sides of the above equations by $\dot{Q}_1(0)$ and $\dot{Q}_2(0)$
and performing the ensemble average, we obtain a system of four
equations for the velocity correlation functions $F_{11}(t)$, $F_{22}(t)$,
$F_{12}(t)$ and $F_{21}(t)$, which in turn, by taking the Laplace-Fourier
transform, give us the coupled equations

$$\left(i\omega + \beta_1[\omega] + \bar{\Omega}_1^2 M_1[\omega] \right) F_{11}[\omega] - \frac{1}{m_1} N_{12}[\omega] F_{21}[\omega] = kT_0/m_1^2 , \tag{28.a}$$

$$\left(i\omega + \beta_2[\omega] + \bar{\Omega}_2^2 M_2[\omega] \right) F_{22}[\omega] - \frac{1}{m_2} N_{12}[\omega] F_{12}[\omega] = kT_0/m_2^2 , \tag{28.b}$$

$$\left(i\omega + \beta_1[\omega] + \bar{\Omega}_1^2 M_1[\omega] \right) F_{12}[\omega] - \frac{1}{m_1} N_{12}[\omega] F_{22}[\omega] = 0 , \tag{28.c}$$

$$\left(i\omega + \beta_2[\omega] + \bar{\Omega}_2^2 M_2[\omega] \right) F_{21}[\omega] - \frac{1}{m_2} N_{12}[\omega] F_{11}[\omega] = 0 . \tag{28.d}$$

Again, we have used the fluctuation theorem and assumed a white-
noise : $F_{ij}(0) = \delta_{ij} kT_0/m_i$ and $\langle \dot{Q}_i(0) f_i^R(t) \rangle = 0$.

The solutions of Eq.(28) are straightforward, where by Cramer's rule we obtain

$$F_{11}(\omega) = kT_0 \, C_2/(m_2 D),$$ (29.a)

$$F_{22}(\omega) = kT_0 \, C_1/(m_1 D),$$ (29.b)

$$F_{12}(\omega) = F_{21}(\omega) = kT_0 \, 1/(\omega^2 D),$$ (29.c)

$$D = m_1 m_2 \, C_1 C_2 - N_{12}^2(\omega),$$ (29.d)

$$C_{1,2} = i\omega + \beta_{1,2}(\omega) + \Sigma_{1,2}^2 \, M_{1,2}(\omega) + N_{12}(\omega)/m_{1,2}.$$ (29.e)

In principle, for given forms of the memory functions $\beta_i(t)$, $M_i(t)$ and $N_{12}(t)$ we shall be able to compute their Laplace-Fourier transforms and thus obtain the line shape function.

For tractable results, let us investigate the Markovian processes and the memory functions with the following forms:

$$\beta_i(t) = \beta_i \, \delta(t),$$ (30.a)

$$M_i(t) = exp(-\gamma_i t),$$ (30.b)

$$N_{12}(t) = \lambda_{12} \, exp(-\gamma_{12} t),$$ (30.c)

where β_i and γ_i represent the line broadening of the active modes achieved by the T_1 (energy) and T_2 (phase) relaxation, respectively, and γ_{12} is the reciprocal correlation time of the interaction between these two active modes with the mode-mode coupling strength λ_{12} related to the interaction potential $V(Q_1,Q_2)$ by $2\lambda_{12} = (\partial^2 V/\partial Q_1 \partial Q_2)_0$. Substituting the Laplace-Fourier transforms of the above memory functions into Eq.(29), the real parts of the results give us the averaged power absorption [from Eq.(24)]

$$\overline{\langle \frac{d\mathcal{E}}{dt} \rangle} = P(T_0) \sum_{i=1}^{2} g_i E_i I_i(\omega) , \tag{31}$$

where

$$I_{i,2}(\omega) = \frac{(\gamma_{i,2} G_{i,2} - \omega H_{i,2}) Z_1 + (\omega G_{i,2} + \gamma_{i,2} H_{i,2}) Z_2}{Z_1^2 + Z_2^2} , \tag{32}$$

with

$$G_{1,2} = R A_{2,1} - 2\omega \gamma_{12} B_{2,1} , \tag{33.a}$$

$$H_{1,2} = R B_{2,1} + 2\omega \gamma_{12} A_{2,1} , \tag{33.b}$$

$$Z_{1,2} = R L_{1,2} \mp 2\omega \gamma_{12} L_{2,1} , \tag{33.c}$$

$$L_1 = A_1 A_2 - B_1 B_2 , \tag{33.d}$$

$$L_2 = A_1 B_2 + A_{12} B_1 , \tag{33.e}$$

$$A_{1,2} = \beta_{1,2} (\gamma_{12} \gamma_{1,2} - \omega^2) - \omega^2 (\gamma_{12} + \gamma_{1,2}) + \bar{\Omega}_{1,2}^2 \gamma_{12} + \lambda_{12} \gamma_{1,2} / m_{1,2} , \tag{33.f}$$

$$B_{1,2} = \omega [\gamma_{12} \gamma_{1,2} - \omega^2 + \beta_{1,2} (\gamma_{12} + \gamma_{1,2}) + \bar{\Omega}_{1,2}^2 + \lambda_{12} / m_{1,2}] , \tag{33.g}$$

$$R = \gamma_{12}^2 - \omega^2 . \tag{33.h}$$

The above line shape, while complicated, is a rather general response function of a system with two coupled active modes and enables us to describe the dynamical nature of LSSP, where both the memory effects of the dephasing kernel (governed by γ_1 and γ_2) and the mode-mode interaction (governed by γ_{12}) are included. Using these expressions [Eqs.(31)-(33)], we may generate different line shapes by varying the relative magnitudes of the parameters β_i, γ_i, γ_{12} and λ_{12}. Since the experimental results of LSSP are not available to date, we shall not show here the numerical plots of the line shapes for an actual system. However, some important features are pointed out as follows: (i) the line shape described by Eq.(31) is essentially composed of two Lorentzian-type line

shapes (with the asymmetry due to the dephasing γ_2) where the peak values are located near the frequencies of the active modes; (ii) the overall line shape is not only characterized by the coupling strength λ_{12} (which governs the interference term in $I_{1,2}(\omega)$] but also by the frequency separation of these two active modes $(\Omega_1 - \Omega_2)$; and (iii) for the very weak coupling case $(\lambda_{12} \approx 0,$ due to the big separation between the frequencies of the active modes) with the laser frequency near resonant to one of the active mode frequency, Eq.(31) reduces to the single-mode line shape [Eq.(21)].

IV. Multiphonon Processes and Laser-Selective Effects

In this section we shall present a classical model to study the nature of the laser-selective effects via the multiphonon processes which have been recently developed by quantum models. For an N-atom polyatomic molecule chemisorbed on a solid surface, the number of "frustrated" vibrational normal modes is 3N. We now divide these 3N intramolecular modes into two types: the active (A) mode(s) and the inactive surface-phonon (B) modes. The bulk-phonon modes with lower frequencies are considered to provide the bath (C) modes for the (A + B) modes. In this picture, the laser photon energy is first deposited into the active (A) mode, and gradually leaks from this mode to the B and C modes accompanied by some energy feedback from the B modes. We then may define the laser-selective excitation (or local heating) in a nonequilibrium fashion, where the selectively excited A mode (or the local heating of the B modes) store the photon energy in the specific vibrational degrees of freedom on a time scale long enough for the related

chemical reaction or the bond breaking to occur.

In previous papers,[5,6] we have discussed this excitation nature (selective, local heating and nonselective thermal heating) by the dynamical energy populations of the system. It was shown that the laser-selective effects are characterized by the pumping rate and the energy relaxation rates of the A and B modes, where the intramolecular vibrational relaxation (IVR) plays an important role in the selective excitation of the A mode and local heating of the B modes. The vibrational level width induced by IVR via multiphonon processes is given by[8,17,18]

$$\Upsilon = 2\pi \sum_{\nu} |G_{\nu}|^2 n_{\nu} \, \delta\left(\Omega_A - \sum_{j} l_j \Omega_j\right), \qquad (34.a)$$

$$n_{\nu} = \prod_{j}\left(\langle n_j \rangle + 1\right) - \prod_{j} \langle n_j \rangle . \qquad (34.b)$$

$\langle n_j \rangle$ is the thermally-averaged Boson occupation number of the j-th mode (with frequency Ω_j) which is strongly coupled to the active mode; G_{ν} measures the strength of the multiphonon coupling and is proportional to the (p+1)-th derivative of the intramolecular anharmonic coupling potential (for a p-order multiphonon process) evaluated at the equilibrium point; and the Dirac delta function simply implies the conservation of energy as in the Fermi golden rule.

We now find, by a fully classical model, the required condition for a slow IVR rate (i.e., a small damping γ), which in turn gives us the possibility of selective bond breaking. We begin with the nonlinear coupled equations of motion of the normal coordinates Q_A (for the active mode) and Q_j (for the bath modes):

$$\ddot{Q}_A(t) + \Omega_A^2 Q_A(t) = \lambda^{(p)} \prod_{j=1} Q_j^{\ell_j}/m_A , \qquad (35.a)$$

$$\ddot{Q}_j(t) + \Omega_j^2 Q_j(t) = \lambda^{(p)} Q_A Q_1^{\ell_1} Q_2^{\ell_2} \cdots Q_j^{\ell_j-1}/m_j . \qquad (35.b)$$

$\lambda^{(p)}$ is the p-phonon coupling constant related to the derivative of the mode-mode interaction potential, V, by

$$\lambda^{(p)} = \left[1/(p+1)! \right] \left[\partial^{p+1} V/\left(\partial Q_A \prod_{j=1} \partial Q_j^{\ell_j} \right) \right]_0 , \qquad (35.c)$$

and $p = \sum_j \ell_j$ (ℓ_j=integer) is the order of the multiphonon coupling, i.e., the active-mode energy gradually leaks into the bath modes by exciting p phonons (ℓ_j phonons of the j-th mode with frequency Ω_j, etc.). With the boundary conditions $Q_A(0)\dot{Q}_A(0) \neq 0$, $Q_j(0) = A_j$ and $\dot{Q}_j(0) = 0$, we shall find the condition (or the relation among the frequencies of the intramolecular modes) for the energy initially stored in the active (A) mode to be significantly transferred to the bath modes. The coupled equations may be solved by an iterative scheme provided the multiphonon coupling may be treated as a small perturbation. Note that the perturbative method is usually valid if one considers a high-order multiphonon process where the coupling strength $\lambda^{(p)}$ is a strongly decreasing function of p.[7,8] For the strong coupling case, e.g., (linear) single-phonon process, we must solve the coupled equations exactly.

By substituting the zero-th order solution $Q_j^{(0)}(t) = A_j\cos(\Omega_j t)$ into Eq.(35.a), we obtain the first-order solution for $Q_A(t)$:

$$Q_A^{(1)}(t) = Q_A(0) \cos(\Omega_A t) + [\dot{Q}_A(0)/\Omega_A] \sin(\Omega_A t) + I(t) , \qquad (36.a)$$

$$I(t) = \lambda^{(p)} \int_0^t dt' \prod_j A_j^{\ell_j} \cos^{\ell_j}(\Omega_j t') \sin[\Omega_A(t-t')] . \qquad (36.b)$$

The integral $I(t) \propto \lambda^{(p)}$, characterizing the strength of the multi-phonon coupling, is quite complicated for arbitrary values of the integers ℓ_j. For simplicity and without losing the spirit of our resonant condition, let us consider the p-phonon process with $\Omega_1 \approx \Omega_2 \cdots \approx \Omega_j$ and $\ell_1 = \ell_2 \cdots = \ell_j$. The coupling integral then appears as

$$I(t) \propto \sum_{k=0}^{p} \frac{\lambda^{(p)}}{\Omega_A^2 - (p-2k)^2 \Omega_j^2} , \qquad (37)$$

which clearly indicates that as $\lambda^{(p)} \to 0$, then $I(t) \to 0$, unless the exact "internal resonant" condition is fulfilled, i.e., $\Omega_A = |p-2k|\Omega_j$ (where p and k are integers). However, when the coupling strength $\lambda^{(p)}$ has a small finite value, the coupling integral $I(t)$ will be significant when Ω_A is near "internal resonant" to Ω_j, i.e., $\Omega_A \approx |p-2k|\Omega_j$. Thus the necessary condition of the IVR to be significant is the near "internal resonant" condition, which is somehow a weaker condition than that of the exact resonant condition governed by the delta function [Eq.(34)]. In fact, if we approximate the upper time of the coupling integral [Eq.(36.a)] from zero to infinite, we obtain the delta function $\delta[\Omega_A - (p-2k)\Omega_j]$.

Therefore, the rate of IVR is restricted by two factors: (i) a low order of the multi-quantum processes and (ii) the near "internal resonant" condition, i.e., $\Omega_A - \sum_j \ell_j \Omega_j \approx 0$. This means that a rapid IVR rate (i.e., a large line broadening which reduces the energy absorption rate) may be achieved only when both of the above

conditions are fulfilled; otherwise, we expect a much slower IVR
rate which in turn cuts off the line broadening and makes the
selective bond breaking possible.

V. Discussion and Conclusion

In our previous work,[5,6] we have investigated the selective
versus nonselective nature of LSSP in terms of parameters such
as the pumping rate, coupling factor and damping rate. We shall
now present some possible physical systems exhibiting selective
effects and surface-enhanced bond breaking.

Let us consider a system which may be pictured as a set of
groups in the frequency domain. For simplicity, we shall consider
the case of only two groups, A and B, in which group A is referred
to as the excited broup which consists of the active mode plus
some intramodes of the adspecies coupled strongly to the pumped
mode, and group B consists of the remaining modes of the total
system (adspecies plus solid). Depending on the relative magni-
tudes of the intragroup (R^{intra}) and the inter group (R^{inter})
coupling rates, which characterize the energy randomization rate
within and between the group(s), respectively, and the laser pump-
ing rate (V), we may introduce several types of laser excitations:
(i) mode (bond)-selective, (ii) molecule-selective and (iii) non-
selective thermal processes.

For LSSP to be characterized as a selective type (mode- or
molecule-selective), we shall require the pumping rate to be faster
than the energy relaxation rate(s), i.e., $V > R^{intra}$ and/or
$V > R^{inter} >> R^{intra}$. For the case of very high (low) pumping (re-
laxation) rate, $V >> R^{intra}, R^{inter}$, a mode-selective type excitation
would be possible. However, for low intensity excitations, the

mode-selective seems to be less likely than the molecule-selective where only the condition required is V, $R^{intra} >> R^{inter}$. By the concept of the "energy-gap law," it is highly possible for a system to have very weak intergroup coupling but strong intragroup coupling, e.g., a large molecule adsorbed on a solid surface like SF_6-metal and a long chain adspecies like A-B-C-D-metal. In these systems the vibrational stretch of the excited species (which is not directly connected to the surface) may behave like a small subsystem, where the excited bond coordinate is composed by the normal coordinates of the related group. This selectively-excited adspecies, while strongly coupled within the group, is weakly coupled to the remaining species (or functional group) of the system. Therefore, selective bond breaking of adspecies (or certain functional group) will be possible.

Another important feature of selective bond breaking of a heterogeneous system (and usually not present in a gas-phase homogeneous) is the surface-enhanced local field acting on the adspecies. The pumping rate could be actually enhanced by a significant factor when the local field is increased due to surface effects such as roughness and electron transfer of the substrate. By the simple relation of the pumping rate and the local electric field $I \propto (E_{loc})^2$, we are able to see that the required laser intensity for selective excitation may be reduced to a factor of 10^8 when the local electric field is enhanced by a factor of 10^4. We note that the enhancement of the local surface field which governs the experimental evidences of surface-enhanced Raman scattering shall

also play an essential role in LSSP, where considerably lower laser intensities (10-10^3 W/cm^2) are used as compared with that of photo-dissociation of polyatomic molecule.

In conclusion, we should mention that selective laser-stimulated desorption (bond breaking) processes are characterized not only by the coherent nature of the laser radiation but also by the hetero-geneity of the substrate (e.g., roughness, orientation and charge transfer) and, very likely, by the internal excitation structure of the pumped state (e.g., the migration-induced and vibration-trans-lation-coupled quasi-continuum state near the desorption region).

We finally note that the excitation nature of LSSP is characterized by the dominant one (or more) component of the above (i) - (iii) processes, which in turn is governed by the relative magnitudes of the pumping rate, the T_1 and T_2 relaxa-tion rate and the dynamical behavior of the excited modes (via the memory effects of GLE).

Appendix

Consider a system of N IR active modes with the initial quantum state $|k\rangle$, which interacts with an electric field of frequency ω, resulting in transitions to some final quantum state $|k'\rangle$. Let the laser radiation be linearly polarized in the z direction, whereby we write the laser monochromatic field as

$$E(t) = E_0 \cos(\omega t), \qquad (A.1)$$

where E_0 is the amplitude of the field. We assume here that the field is spatially uniform, since the wavelength is large compared to the dimensions of the adspecies. The interaction Hamiltonian between the field and the adspecies can be written as

$$H'(t) = \sum_i \mu_i E_i \cos(\omega t), \qquad (A.2)$$

where E_i is the effective amplitude of the electric field acting on the i-th normal modes with the active dipole moment operator μ_i.

According to time-dependent perturbation theory, the transition probability of a transition from the state $|k\rangle$ to the state $|k'\rangle$ is given by[19]

$$P_{k'k}(t) = \left| \langle k'|\Psi(t)\rangle \right|^2 = \frac{1}{\hbar^2} \left| \int_0^t dt' \, e^{i\Omega_{k'k}t'} \langle k'| H'(t')|k\rangle \, e^{\eta t'} \right|^2, \qquad (A.3)$$

where $\Omega_{k'k} = \Omega_{k'} - \Omega_{k}$, and the laser field is turned on slowly with an $\exp(\eta t)$ factor (with $\eta \to 0^+$). Using the expression for the interaction Hamiltonian $H'(t)$ [Eq.(A.2)] and working out the integral of Eq.(A.3), we obtain the transition rate (i.e., the transition probability per unit time) as

$$W_{k'k}(t) = \frac{d}{dt} P_{k'k}(t)$$

$$= \frac{1}{4\hbar^2} \left| \langle k' | \sum_i \mu_i E_i | k \rangle \right|^2 \times \tag{A.4}$$

$$\left\{ \left[\frac{2\gamma}{(\Omega_{k'k}-\omega)^2+\gamma^2} + \frac{2\gamma}{(\Omega_{k'k}+\omega)^2+\gamma^2} \right] (1-\cos 2\omega t) + \left[\frac{2(\omega-\Omega_{k'k})}{(\Omega_{k'k}-\omega)^2+\gamma^2} + \frac{2(\omega+\Omega_{k'k})}{(\Omega_{k'k}+\omega)^2+\gamma^2} \right] \sin(2\omega t) \right\},$$

which is still time dependent. However, we shall be interested in
the time-averaged quantity (over the field cycle $T = 2\pi/\omega$). Using
the fact that the time average of the terms $\sin(2\omega t)$ and $\cos(\omega t)$
vanish and transforming the rhs of Eq.(A.4) into the Dirac delta
function,

$$\lim_{\gamma \to 0} \left[\frac{2\gamma}{(\Omega_{k'k} \pm \omega)^2 + \gamma^2} \right] = 2\pi \delta(\Omega_{k'k} \pm \omega) , \tag{A.5}$$

we obtain the time-averaged transition rate (which is now time
independent) as

$$\overline{W}_{k'k} = \frac{\pi}{2\hbar^2} \left| \langle k' | \sum_i \mu_i E_i | k \rangle \right|^2 \left[\delta(\Omega_{k'k}-\omega) + \delta(\Omega_{k'k}+\omega) \right]. \tag{A.6}$$

We then may calculate the time-averaged energy absorption
rate of the system given by

$$\overline{\langle \frac{d\varepsilon}{dt} \rangle} = \sum_{k'} \sum_k P_k \hbar \Omega_{k'k} \overline{W}_{k'k} , \tag{A.7}$$

where p_i is the probability that the system was in the initial state
$|k\rangle$. Since the summations over k and k' range over all the quantum
states of the system, we may interchange these indices in the sum-
mation over the second delta function in Eq.(A.5) to obtain

$$\overline{\langle \frac{d\varepsilon}{dt} \rangle} = \frac{\pi}{2\hbar} \sum_{k'} \sum_k \Omega_{k'k} (p_k - p_{k'}) \left| \langle k' | \sum_i \mu_i E_i | k \rangle \right|^2 \delta(\Omega_{k'k}-\omega) . \tag{A.8}$$

By assuming the system initially to be in thermal equilibrium, we
can relate the thermal probabilities of the system p_k and $p_{k'}$ by

$$P_{k'} = P_k \cdot exp(-\beta \hbar \Omega_{k'k}) , \qquad (A.7)$$

where $\beta = (kT_0)^{-1}$ and T_0 is the initial temperature of the system. In order to convert Eq.(A.8) to the Heisenberg picture, we introduce the Fourier transform of the delta function,

$$\delta(\Omega_{k'k} - \omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i(\Omega_{k'k} - \omega)t} \cdot dt \quad . \qquad (A.10)$$

Using the expressions of Eqs.(A.9) and (A.10), Eq.(A.8) becomes

$$\overline{\left\langle \frac{d\mathcal{E}}{dt} \right\rangle} = \frac{\omega}{4\hbar}(1 - e^{-\beta\hbar\omega}) \sum_{k'k} P_k \langle k| \sum_i \mu_i E_i |k'\rangle \langle k'| \sum_j \mu_j E_j |k\rangle \int_{-\infty}^{\infty} dt \, e^{i(\Omega_{k'k} - \omega)t} . \qquad (A.11)$$

Since the $|k\rangle$ and $|k'\rangle$ are eigenstates of the unperturbed system [i.e., $H'(t) = 0$], we have

$$e^{-i\Omega_k t} |k\rangle = U(t) |k\rangle , \qquad (A.12)$$

$$\langle k'| e^{i\Omega_{k'}t} = \langle k'| U^{\dagger}(t) , \qquad (A.13)$$

where $U(t) = \exp(-iH_0 t/\hbar)$ is a unitary operator of the unperturbed Hamiltonian H_0. Combining Eqs.(A.11), (A.12) and (A.13) and using closure relation of the final state $|k'\rangle$, we obtain

$$\overline{\left\langle \frac{d\mathcal{E}}{dt} \right\rangle} = \frac{\omega}{4\hbar}(1 - e^{-\beta\hbar\omega}) \int_{-\infty}^{\infty} dt \, e^{-i\omega t} \langle \sum_{i,j} \mu_i(t)\mu_j(0) \rangle . \qquad (A.14)$$

where $\mu_i(t)$ is the dipole moment of the i-th active mode defined in the Heisenberg picture by

$$\mu_i(t) = U^{\dagger}(t) \, \mu_i(0) \, U(t) \qquad (A.15)$$

$\langle \cdots \rangle$ denotes the ensemble average, i.e., in writing Eq.(A.14), we have used the equilibrium ensemble average

$$\sum_k P_k \langle k| \mu(t)\mu(0) |k\rangle \equiv \langle \mu(t)\mu(0) \rangle . \qquad (A.16)$$

Thus, we have shown that the time-dependent (time and ensemble) averaged energy absorption rate [Eq.(A.14)] is characterized by the initial temperature T_0 of the system and the Fourier transforms of the time-correlation function of the dipole-moments of the absorbing adspecies in the absence of the laser field.

In order to employ GLE which gives the correlation function of the velocity, we shall further express the averaged absorption rate in terms of the velocity correlation. To do this, let us expand the dipole moment in terms of the related normal coordinates

$$\mu_i(t) \approx \mu_{io} + \mu_{io}' \cdot Q_i(t) + \cdots \qquad (A.17)$$

which gives us

$$\langle \mu_i(t)\mu_j(0) \rangle \approx q_i q_j \langle Q_i(t) Q_j(0) \rangle, \qquad (A.18)$$

where q_i, q_j are the effective classical charges. Here we have used $q_i = \mu_{io}'$, $q_{j'} = \mu_{jo}'$ and dropped the μ_{io} , μ_{jo} terms which are related to the pure rotational transitions and give no contributions to the vibrational excitation processes (by the selection rule). Substituting of Eq.(A.18) into Eq.(A.14) and using the relation between the displacement correlation and the velocity correlation $\langle \dot{Q}(t)\dot{Q}(0) \rangle = \omega^2 \langle Q(t)Q(0) \rangle$, we obtain

$$\overline{\left\langle \frac{d\mathcal{E}}{dt} \right\rangle} = \frac{1}{2k\omega}(1 - e^{-\beta\hbar\omega}) \sum_{i,j} \left(q_i q_j E_i E_j \right)\left(Re\, F_{ij}[\omega] \right), \qquad (A.19)$$

where $Re\, F_{ij}[\omega]$ is the real part of the Laplace-Fourier transform of the velocity correlation function defined by

$$F_{ij}[\omega] \equiv \int_0^\infty dt\, e^{-i\omega t} F_{ij}(t) , \quad F_{ij}(t) = \langle \dot{Q}_i(t) Q_j(0) \rangle. \quad (A.20)$$

We note that the velocity correlation function is even in time, i.e., $F_{ij}(-t) = F_{ij}(t)$.

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$\langle \cdots \rangle$ denotes the ensemble average, i.e., in writing Eq.(A.14), we have used the equilibrium ensemble average

$$\sum_{k} p_k \langle k | \mu(t)\mu(0) | k \rangle \equiv \langle \mu(t)\mu(0) \rangle . \qquad (A.16)$$

the velocity correlation function defined by

$$F_{ij}[\omega] \equiv \int_0^{\infty} dt \, e^{-i\omega t} F_{ij}(t) \quad , \quad F_{ij}(t) = \langle \dot{Q}_i(t) \, Q_j(0) \rangle \, . \quad (A.20)$$

We note that the velocity correlation function is even in time, i.e., $F_{ij}(-t) = F_{ij}(t)$.